I. The Equilibrium in Liquid Mixtures of Ammonia and Xylene

II. The Molecular Weight of Complex Sodium Tellurides in Liquid Ammonia

BY

EDWARD H. ZEITFUCHS

A DISSERTATION

SUBMITTED TO THE FACULTY OF CLARK UNIVERSITY, WORCESTER, MASS., IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY, AND ACCEPTED ON THE RECOMMENDATION OF CHARLES A. KRAUS

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I. THE EQUILIBRIUM IN LIQUID MIXTURES OF AMMONIA AND XYLENE

Introduction

Franklin and Kraus have observed that mixtures of ammonia and *meta*-xylene have an upper critical end-point[1] a little below room temperatures. Since the vapor-pressure curves of only a few such systems have been studied thus far,[2] it appeared worth while to investigate this system in some detail. In as much as the vapor pressure of xylene is low compared with that of ammonia, the total-pressure curves will differ little from the partial-pressure curves.

In the present investigation the vapor pressure of various liquid mixtures has been determined together with the composition of the liquid phases of the monovariant system. The latter data were determined in a separate series of experiments.

The critical end-point was determined in a special experiment by direct observation of the temperature at which the two phases become identical. For this purpose ammonia and *meta*xylene were sealed in a heavy walled

[1] This is sometimes called the critical point of solution. Since such a point also occurs in the diphase system, it appears preferable to designate the critical point of the three-phase system as critical end-point, as has been suggested by Büchner.

[2] The literature relating to systems of this type has been collected by Büchner in Part 2, Vol. II, of Roozeboom's "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," and detailed references may accordingly be omitted here.

glass tube provided with an electromagnetic stirrer. This tube was placed in a bath, contained in a Dewar tube, the temperature of which was allowed to rise slowly. Keeping the mixture vigorously stirred, the temperature was noted at which the two-phase system disappeared. The mean value so found for the critical end-point was 14.7°.

The Vapor Pressure of Liquid Mixtures of Ammonia and Xylene

Apparatus.—The boiling point of the *meta*xylene used in this work was found to be close to 139.2°, the value given in Landolt-Börnstein's Tables of Physico-chemical Constants for the boiling point of pure *m*-xylene. The ammonia was drawn from a container in which it had been purified by the method given by Franklin and Kraus.[3] The arrangement of the apparatus used to measure the total pressure of the vapor of mixtures of liquid ammonia and liquid xylene is shown in Fig. 1.

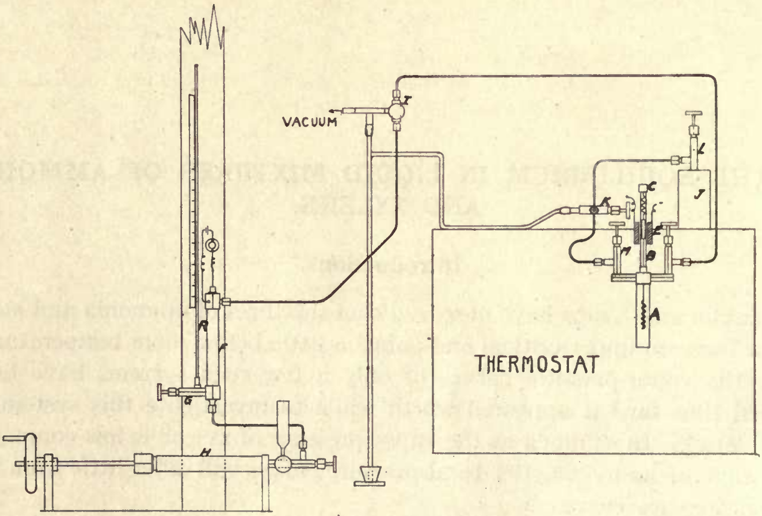

Fig. 1.—The apparatus employed in determining the vapor pressure of the monovariant system.

All parts of the apparatus which were under pressure were constructed of metal, with the exception of the mercury column *R*, which was made of glass tubing of 1 mm. thickness and 4 mm. internal diameter.

The liquid mixture was contained in a thin walled steel tube *A* of 2.75 cm. internal diameter and 15 cm. length. This tube was suspended in a thermostat containing kerosene which was vigorously stirred and whose temperature could readily be controlled within 0.01°. The total volume of the liquid mixture in Tube *A* varied from 30 cc. to 70 cc., depending on the composition. A brass tube, *B*, 12 mm. o. d. by 9 mm. i. d., and 20 cm. long, was screwed and soldered to *A*. A steel core, having a diameter of 8 mm. and a length of 7.5 cm. was supported in the bore of the brass tube by a steel piano wire spring of No. 31 B. and S. gage. This spring was fastened to the brass cap *C* which was

[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 284 (1900).

screwed into a conical seat on the top of the tube A. A plunger stirrer was suspended from the steel core by means of a heavy steel wire. The core was actuated by means of a solenoid E in which the current was interrupted once per second by means of a motor driven contact breaker. The degree of stirring could be regulated by adjusting the position of the solenoid along the axis of the brass tube and by resistance placed in the solenoid circuit.

Connection was made with the manometer R by means of a mercury reservoir F of thin walled steel tubing of 27 mm. i. d. and 17.5 cm. length. To its ends were welded 2 short pieces of hexagonal steel which were machined to take the various connections. Connection with the mercury column was made through the valve G. The column had a height of 7.2 meters. A plug carrying an insulated platinum contact point was screwed into the top of F. By means of this contact point, which projected into a small opening near the top of the mercury reservoir, the level of the mercury could be maintained at a fixed point with ease and precision. The position of the platinum point was transferred to a point on a steel tape suspended alongside the manometer column. Contact of the mercury with the platinum point was indicated by means of a small electric lamp. The amount of mercury in the reservoir was regulated by means of the mercury displacement piston H.

Connection between the tube A, containing the liquid ammonia-liquid xylene, and the mercury reservoir F, was made by means of a small bore steel tube as shown. This capillary steel tube connection was provided with a valve at I, by means of which the space above the mercury in the reservoir and the tube F and in the connecting tube could be evacuated.

The ammonia supply was contained in a light steel cylinder J. The steel capillary tube connecting this container and the tube A could be evacuated at will through the valve K. The desired quantity of ammonia was distilled from the container J into the tube A on opening valves L and M. During the distillation, the temperature of the thermostat was maintained near 8°, while the ammonia container was slightly warmed by resting it on a small electrically heated plate. The quantity of ammonia, which distilled into A, was obtained by difference in the weight of the container before and after the distillation.

The description of the method of determining the total vapor pressure of a mixture of liquid xylene and liquid ammonia by means of this apparatus follows.

Experimental Method.—For a mixture of a desired composition, the proper amount of xylene was introduced into A through B by means of a weight pipet having a long stem. B was then closed by Cap C, and A was evacuated. The desired quantity of ammonia was next distilled into A from J in the manner described above. The plunger stirring the liquid in A was then set in motion and the temperature of the bath was brought to the value desired.

The valve G connecting the mercury column and the mercury reservoir was then cautiously opened and the column allowed to adjust itself to the pressure in the apparatus, after which mercury was forced into the reservoir by means of the displacement piston H until contact was made with the platinum point. The position of the top of the mercury column was read on a graduated steel tape suspended with its zero point near the top of the column. As soon as the position of the meniscus of the mercury

column became constant, two readings were made at intervals of 10 minutes. The height of the column of mercury was given by the difference in reading of the position of the platinum point and the position of the top of the mercury column. The temperature of the column was obtained from thermometers placed at 120cm. intervals along its height. The barometric height and the temperatures were read for every measurement of the height of the manometer column, and the temperature of the room in the immediate neighborhood of the apparatus was noted. The temperature of the thermostat was then changed to the one next desired and the procedure for measuring the pressure, as just described, was repeated.

In general, for a given composition, the run was started at 8° and measurements of the pressure were made at 8°, 10°, 12°, 14°, 15°, 17° and 20°. In some cases, for a mixture of given composition, the pressure measurements were repeated at the various temperatures as the temperature was varied from 8° to 20° and back from 20° to 8° by the intervals given above. The agreement of the measurements in any such case was found to lie well within the limits of error involved in other parts of the experimental work.

Experimental Results.—In Table I are given in detail the data as obtained for a complete run at some one composition. In Table II are

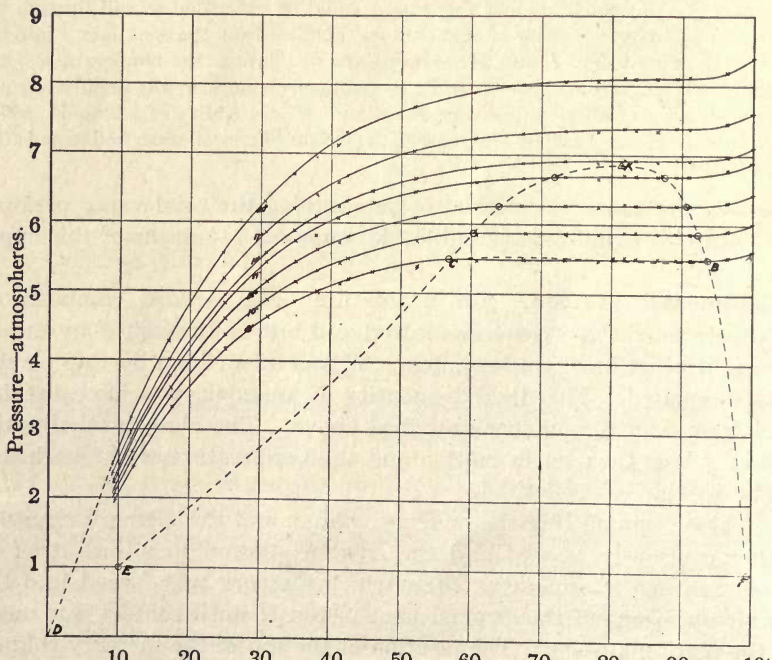

Fig. 2.—Isotherms of the mixtures.

given the values of temperature, pressure, and mean composition for all experiments which were considered satisfactory. It was necessary to correct the total composition of the liquid ammonia-xylene mixtures for the amount of ammonia in the vapor above the liquid in *A* and in the tube connecting this reservoir with *F*. The volume, the pressure and the temperature of the vapor filling this space were in all cases known, and from these data the weight of ammonia in the vapor space was calculated, assuming the laws of perfect gases to hold. While this is far from true for ammonia[4] at these high pressures, yet the error introduced was negligible, since the correction for ammonia in the vapor was in any case small compared with the total amount of ammonia present. This correction has been applied to the compositions given in Table II.

The temperatures given in Tables I, II and IV are subject to the corrections indicated in Table III, which were obtained by comparing the laboratory thermometer used in this investigation with a thermometer standardized by the Reichsanstalt.

TABLE I

DETAILED DATA FOR A RUN

Run No. 6. Position of platinum point (transferred to steel tape), 22.917 ft.

Temperature of Thermostat[a]	Position of top of mercury column on steel tape	Height of mercury column	Average temp. of mercury column	Height of mercury column corrected for temp.[b]	Barometer corrected for temp.	Pressure of mixed xylene-ammonia vapors	
° C.	Ft.	Cm.	° C.	Cm.	Cm.	Cm.	Atm.
8	20.375	77.48	23	77.19	72.89	150.08	1.975
10	20.167	83.82	25	83.49	72.92	156.41	2.058
12	19.962	90.07	25	89.71	72.98	162.69	2.141
14	19.750	96.53	26	96.11	72.97	169.08	2.224
15	19.641	99.85	26	99.43	72.97	172.40	2.268
17	19.416	106.70	26	106.25	72.98	179.23	2.358
20	19.078	117.00	26	116.52	72.99	189.51	2.493

[a] Temperature subject to corrections given in Table III.

[b] Corrections obtained from "Physikalische-Chemische Tabellen" by Landolt-Börnstein.

In Fig. 2 the pressures given in Table II are plotted as ordinates against the temperatures as abscissas. The horizontal portions of the isotherms represent the mean composition of the mixture for which 2 liquid phases are present. The end-points of the horizontal portions give the composition of the 2 liquid phases in equilibrium with each other. These points, at which the isotherms become horizontal, can be estimated only roughly from the plots. As it was desirable to know the composition of the 2 liquid phases somewhat more accurately, a separate set of experiments was carried out for their determination.

[4] Lange, *Z. angew. Chem.*, **1903**, pp. 511–13.

TABLE II

VAPOR PRESSURE AND MEAN COMPOSITION OF MIXTURES AT DIFFERENT TEMPERATURES

Temperature of thermostat[a] ° C.	Pressure of mixed xylene-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia	Pressure of mixed xylene-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia	Pressure of mixed xylene-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia
	Run 4		Run 5		Run 6	
8	4.64	31.0	3.32	17.5	1.97	9.5
10	4.89	30.9	3.47	17.4	2.06	9.5
12	5.15	30.9	3.59	17.3	2.14	9.5
14	5.43	30.8	3.76	17.3	2.22	9.4
15	5.56	30.8	3.85	17.2	2.27	9.4
17	5.86	30.8	4.01	17.2	2.36	9.3
20	6.30	30.7	4.27	17.1	2.49	9.3
	Run 8		Run 9		Run 11	
8	2.46	12.0	4.16	25.2	4.87	35.2
10	2.57	11.9	4.37	25.1	5.14	35.1
12	2.67	11.9	4.60	25.0	5.43	35.0
14	2.79	11.8	4.83	25.0	5.73	35.0
15	2.85	11.8	4.94	25.0	5.88	34.9
17	2.97	11.8	5.19	24.9	6.20	34.8
20	3.15	11.7	5.56	24.8	6.70	34.8
	Run 12		Run 13		Run 14	
8	5.01	38.1	5.18	42.6	5.29	46.1
10	5.31	38.1	5.49	42.5	..	..
12	5.61	38.0	5.81	42.5	..	..
14	5.92	37.9	6.14	42.3	6.30	46.1
15	6.10	37.9	6.31	42.2	6.46	45.9
17	6.40	38.0	6.68	42.4	..	..
20	6.93	37.9	7.31	42.2	..	..
	Run 15		Run 16		Run 17	
8	5.42	50.1	5.43	54.2	5.48	64.6
10	5.70	50.2	..	..	..	..
	Run 18		Run 19		Run 20	
8	5.48	78.1	5.50	86.5	5.51	89.1
10	5.86	78.1	5.87	86.5	5.88	89.1
12	6.25	78.1	6.28	86.6	6.29	89.1
14	6.66	78.1	6.70	86.6	6.70	89.1
15	6.89	78.0	6.91	86.5	6.93	89.1
17	7.34	78.0	7.36	86.4	7.39	89.1
20	8.06	78.0	8.10	86.4	8.10	89.1
	Run 21		Run 22		Run 23	
8	5.50	91.2	5.54	96.4	5.62	Pure ammonia
10	5.86	91.1	5.92	96.3	6.02	Pure ammonia
12	6.28	91.1	6.33	96.3	6.44	Pure ammonia
14	6.70	91.0	6.79	96.3	6.90	Pure ammonia
15	6.92	91.0	6.98	96.3	7.11	Pure ammonia
17	7.39	90.9	7.46	96.3	7.60	Pure ammonia
20	8.13	90.8	8.19	96.3	8.39	Pure ammonia

	Run 24		Run 26		Run 28	
8	5.60	98.7	5.50	95.1	5.37	50.2
10	6.00	98.7	5.88	95.0	..	..
12	6.41	98.7	6.30	95.0	..	..
14	6.86	98.7	6.73	95.0	..	..
15	7.09	98.7	6.95	95.0	..	..
17	7.56	98.7	7.41	95.0	..	..
20	8.33	98.7	8.18	95.0	..	..
	Run 30		Run 31		Run 32	
8	5.12	41.3	5.39	52.3	5.47	60.8
10	5.42	41.3	5.74	52.3	5.84	60.8
12	5.71	41.6	6.09	52.1	6.22	60.7
14	6.06	41.1	6.46	52.1	6.61	60.7
15	6.24	41.1	6.65	52.1	6.82	60.7
17	6.58	41.1	7.05	51.9	7.24	60.6
20	7.13	40.9	7.68	51.9	7.91	60.5
	Run 33		Run 34		Run 35	
8	5.49	67.5	5.50	73.4	5.53	80.2
10	5.86	67.4	5.88	73.4	..	..
12	6.26	67.4	6.28	73.4	..	..
14	6.67	67.4	6.69	73.4	..	..
15	6.88	67.3	6.91	73.4	..	..
17	7.31	67.3	7.35	73.4	..	..
20	8.01	67.3	8.06	73.4	..	..
	Run 36		Run 37			
8	5.53	81.8	5.51	83.4		
10	5.89	81.8	5.89	83.4		
12	6.30	81.8	6.28	83.4		
14	6.72	81.8	6.70	83.4		
15	6.94	81.8	6.92	83.4		
17	7.39	81.8	7.37	83.4		
20	8.12	81.8	8.10	83.4		

[a] All temperatures given in Table II are subject to the corrections given in Table III.

TABLE III

THERMOMETER CORRECTIONS

Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.	Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.
8	7.83	15	14.79
10	9.82	17	16.79
12	11.81	20	19.80
14	13.79	..	...

Composition of the Liquid Phases

Apparatus.—In Fig. 3 is shown the apparatus by means of which the composition of the 2 liquid phases was determined. In a preliminary experiment, the relative volumes of the 2 phases were determined by observations made on mixtures contained in a glass tube of uniform diameter. The mean composition of the liquid mixture used in this preliminary experiment corresponded to that at the critical point, *K*, which was esti-

mated from the plot shown in Fig. 2. The relative volumes of the 2 layers in the glass tube changed only a few per cent. for a temperature change from 8° to 14.7°, the temperature of the critical end-point. With this knowledge of the volumes occupied by the 2 phases of a mixture of known mean composition, the apparatus shown in Fig. 3 was designed. The volumes of the chambers *A*, *B* and *C* were so proportioned that, when in an upright position, the surface separating the two liquid layers should always come within the mid section *B* for temperatures from 8° to 14°.

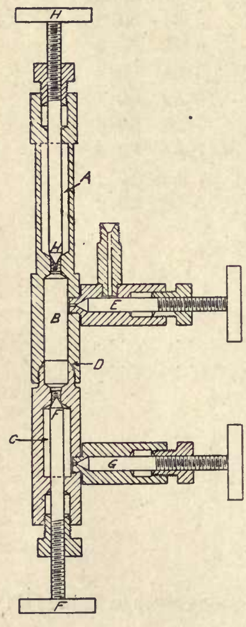

Fig. 3.—Apparatus employed in determining the composition of the liquid phases.

Procedure.—The procedure adopted in making a determination of the composition of the two liquid phases at a given temperature is as follows. The desired quantity of xylene was run into Chamber *C* from a weight pipet. The two parts of the apparatus were then screwed together at the conical joint *D*, and the whole was then placed in the thermostat in an upright position with Chamber *C* at the bottom. The outlet valve *E* was connected by means of a steel tube to the valve *K*, shown in Fig. 1. After evacuation, the desired quantity of ammonia was distilled into the apparatus. The quantity of ammonia introduced was obtained by difference in the weight of the container. Valve *E* was then closed and the whole apparatus was shaken at brief intervals, for a period of half an hour. The apparatus was then allowed to remain at rest for 10 or 15 minutes to allow thorough separation of the layers. Valve *F* was then closed, thus sealing a portion of the lower, heavier layer in Chamber *C*. A valve shown at *G* was next opened to allow for the expansion of the liquid due to temperature rise when the apparatus was removed from the bath. The valve *H* was then closed, sealing a portion of the upper, lighter layer in the chamber *A*. The apparatus was then removed from the bath, the portion in the mid section *B* was discarded through valve *E*, after which the two parts of the apparatus were separated at the conical joint *D*. Each portion of the apparatus was weighed. The ammonia in *A* and *C* was determined by running these portions into known quantities of standard sulfuric acid and titrating back with sodium hydroxide. The empty parts of the apparatus were then again weighed, and the weight of the sample of the liquid layer was obtained by difference.

Experimental Results.—The following are the data in detail as obtained in one of these determinations.

EXPERIMENT 6 AT 12°

Wt. of part of apparatus containing upper portion of xylene-ammonia mixture	481.630 g.
Wt. of apparatus empty	480.326 g.
Wt. of sample of xylene-ammonia	1.304 g.
Vol. of 0.953 N H_2SO_4 neutralized by xylene-ammonia sample	49.89 cc.
Ammonia in sample .... 0.04760 mols ≈	0.810 g.
Xylene in sample .... 0.494 g. ≈	0.00467 mols
Mol per cent. of ammonia	90.3
Wt. of part of apparatus containing lower portion of xylene-ammonia mixture	429.648 g.
Wt. of apparatus empty	427.585 g.
Wt. of sample of xylene-ammonia	2.063 g.
Vol. of 0.953 N H_2SO_4 neutralized by xylene-ammonia sample	27.27 cc.
Ammonia in sample .... 0.0260 mols ≈	0.442 g.
Xylene in sample .... 1.621 g. ≈	0.0153 mols
Mol per cent. of ammonia	63.0

In Table IV are given the results of the determinations of the composition at 8°, 10°, 12° and 14°. In Fig. 2, these values of the composition are represented on their respective isotherms as points surrounded with circles.

TABLE IV

COMPOSITION OF THE TWO LIQUID PHASES AT DIFFERENT TEMPERATURES

Run	Temp. °C.	NH_3 in upper layer %	NH_3 in lower layer %
12	8	93.7	56.5
13	8	93.4	56.8
14	8	93.4	56.8
3	10	92.0	60.5
4	10	92 4	60.3
5	10	91.7	59.5
15	10	92.3	60.4
6	12	90.3	63.0
7	12	90.3	64.0
11	12	90.9	64.3
8	14	87.2	..
9	14	87.2	71.8
10	14	88.1	71.8
Av.	8	93.6	56.7
Av.	10	92.2	60.4
Av.	12	90.5	63.8
Av.	14	87.5	71.8

The composition of the two liquid phases was determined at the boiling point of liquid ammonia at atmospheric pressure by means of another apparatus. In this experiment a known weight of xylene was run into a glass tube which was provided with a stirrer and which was immersed

in liquid ammonia contained in a Dewar flask. After exhausting, ammonia was distilled into the tube until 2 phases appeared, the liquid being vigorously stirred in the meantime. The amount of ammonia distilled over was determined by the change in the weight of the supply container. By this means the composition of the solution rich in xylene was determined.

To obtain the composition of the phase rich in ammonia, the above procedure was repeated, but with a small amount of xylene present at the beginning. The point was noted at which the xylene phase disappeared. From the known weights of xylene and ammonia present, the composition of the phase rich in ammonia was thus found.

It was difficult to determine accurately the appearance of a second phase or the disappearance of the first phase, and the results obtained in this part of the work may be in error by several per cent. The values found were 10.0 mol per cent. of ammonia for the phase rich in xylene, and 0.56 mol per cent. of xylene in the phase rich in ammonia.

The broken line curve shown in Fig. 2, passing through the circles on the isotherms, represents the composition of the liquid phases in equilibrium with each other.

Discussion

The form of the pressure-concentration isotherms shown in Fig. 2 places the system ammonia:*meta*xylene among Büchner's first type,[5] in which the pressure of the 3-phase system lies intermediate between that of the pure components. In general, it has been found that liquid pairs having relatively high boiling points fall within this class, while liquid pairs whose boiling points are comparable fall within the class in which the pressure of the 3-phase system is higher than that of the components.

Büchner has found, as a result of an examination of a large number of systems of this type, that a temperature difference of at least 100° must exist between the boiling points of the two compounds, in order that they should fall within this class. There are, however, several exceptions to this rule. Büchner finds also that the ratio of the critical temperatures of the pairs which belong to this group has a value equal to, or greater than, 1.4. The system ammonia:xylene fulfils both these conditions, the difference in the boiling points being 172.7°, while the ratio of the critical temperatures is 1.41.

Considering the isotherms, the behavior of the mixtures of ammonia and xylene is such as might be expected. At temperatures below the critical end-point, the isotherms appear very much flattened at compositions approaching those of the 2 liquid phases. So, also, above the critical point, the isotherms at compositions in the neighborhood of the critical composition are comparatively flat. This system differs from other systems

[5] Ref. 2, p. 34.

most largely, perhaps, in that the critical region is relatively contracted on one side of the figure. Whereas in many cases the critical composition lies in the neighborhood of 50% of the 2 components, in this system the critical composition has a value of approximately 82 mol per cent. of ammonia. As may be seen from Fig. 2, the composition of the 2 liquid phases diverges largely at lower temperatures, so that at the boiling point of liquid ammonia the phase rich in xylene contains only 10 mol per cent. of ammonia while that rich in ammonia contains only 0.56 mol per cent. of xylene. From the form of the curve, it may be inferred that this system will not exhibit a lower critical end-point. In any case, the freezing point of ammonia is reached at a temperature of approximately $-76°$, and a solid phase thus intervenes. It is doubtful, however, whether this system may be looked upon as having a lower critical end-point, even in the metastable regions.

Very striking is the large deviation of the pressure curves, which in this case are practically identical with the partial pressure curves of ammonia, from Raoult's law at low concentrations of xylene. It is theoretically necessary that, at the ammonia axis, the pressure curves shall become tangent to the straight line joining the pressure of this component with the origin on the opposite side of the diagram. It is evident, from the form of the curves, that the deviations from Raoult's law must be large even at relatively low concentrations. There is thus an intimate relation between the deviations from Raoult's law, that is to say, the deviations of a real system from that of an ideal one, and the appearance of new phases in the system. Our knowledge of the fundamental causes leading to a separation of a system into 2 phases is as yet too limited to enable us to interpret the phenomena observed, but it is clear, even now, that the appearance of new phases involves appreciable deviations from the laws of ideal systems. The greater the difference in the physical properties and constitution of the components in a mixture, the lower is the concentration at which the deviations from ideal systems reach appreciable values; and the lower is the concentration of the second component at which a new phase may appear. This is strikingly illustrated in the case of the system sodium: liquid ammonia, in which a critical phase appears having a composition of approximately 97 mol per cent. of ammonia.[6] This corresponds to a concentration a little above normal.

It follows from the theory of liquid mixtures that the isotherms in the homogeneous regions are two branches of a continuous curve, which represents the pressure of a homogeneous system over the complete concentration range. Between the compositions of the 2 liquid phases, however, the homogeneous states are metastable and unstable, and are therefore

[6] Kraus, *J. Am. Chem. Soc.*, **29**, 1557 (1907). Ruff and Zedner, *Ber.*, **41**, 1948 (1908).

only realizable in part, excepting on the critical isotherm. It has not been found possible thus far to evolve a theory of mixtures sufficiently general in nature to include the case of systems in which one or both of the components are abnormal liquids. It is clear, however, that the theoretical isotherm must exhibit a maximum and a minimum in this region. In the figure, the broken line connecting the points B and C indicates such a form of the curve. It may be inferred, since the isotherms immediately above the critical end-point as well as in the homogeneous regions adjacent to the 3-phase equilibrium are comparatively flat, that the theoretical isotherm throughout the metastable and unstable regions will be comparatively flat.

Summary

1. The total vapor pressure of liquid mixtures of ammonia and *meta*-xylene has been determined for the entire range of compositions at temperatures of 8°, 10°, 12°, 14°, 15°, 17° and 20°. Mixtures of liquid ammonia and *meta*xylene exhibit a critical end-point at 14.7° at a pressure of 6.85 atmospheres and a composition of 81.4 mol per cent. of ammonia.

2. The composition of the liquid phases in equilibrium with each other in the 3-phase system has been determined at the temperatures given above and at −33.5°. At lower temperatures the percentage of ammonia in the phase rich in xylene decreases very markedly with the temperature.

3. The significance of the results obtained is briefly discussed.

II. THE MOLECULAR WEIGHT OF THE SODIUM-TELLURIUM COMPLEX IN LIQUID AMMONIA AS DERIVED FROM VAPOR-PRESSURE MEASUREMENTS

Introduction

As a result of the investigations of Kraus,[1] Posnjak, Smyth,[2] and Kraus and Chiu,[3] the atomic proportions in which sodium appears combined with lead and with tellurium in liquid ammonia solution have been definitely established.

[1] Kraus, *J. Am. Chem. Soc.* **29**, 1556 (1907).
[2] Posnjak, see Smyth, *ibid.*, **39**, 1299 (1917).
[3] Kraus and Chiu, *ibid.*, **44**, 1999, 1922.

In equilibrium with metallic lead, one atom of sodium appears combined with 2.25 atoms of lead in ammonia solution. Smyth has suggested that in solution several lead compounds containing various amounts of lead exist in equilibrium with each other. Since the ratio of lead to sodium appears to be independent of concentration, the equilibrium among the complexes is not displaced by concentration change.

In the case of solutions containing sodium and tellurium, the ratio of tellurium to sodium, varies as a function of the concentration (of sodium), as was shown by Allison,[4] Power[5] and Kraus and Chiu.[3] At a concentration in the neighborhood of 2 N, the ratio of tellurium to sodium has a value of approximately 2.02, and this ratio remains very nearly constant to concentrations as low as 0.5 N, after which it begins to decrease as the concentration decreases.

Kraus and Chiu have investigated the system, sodium-tellurium-ammonia, in some detail and have established the fact that the reaction between sodium and tellurium takes place in several stages. The first product of the reaction is the normal telluride, Na_2Te, which compound further reacts with tellurium to form a solution the composition of which corresponds to the formula Na_2Te_2. The composition of the solution remains fixed so long as the normal telluride is present.[6] In the presence of the free metal (tellurium) the telluride Na_2Te_2 reacts further with tellurium to form a telluride or a mixture of tellurides containing larger amounts of this element. As has already been noted, the ratio of tellurium to sodium in a solution in equilibrium with free metallic tellurium varies with the concentration.

The question naturally arises: What is the nature of the solutions of the complex telluride? It has been shown that, in solutions containing the compounds of sodium and lead and sodium and antimony, the less electronegative element functions as anion, since it may be precipitated in the free state on the anode by electrolysis. In the case of a normal salt, such as the telluride, Na_2Te, there is every reason for believing that in solution the tellurium is present as a normal telluride ion carrying 2 negative charges. When, however, the normal telluride reacts further with tellurium, the question arises: Is a complex anion formed, consisting of the original telluride ion associated with other atoms of tellurium; or, conceivably, does the valence of the tellurium ion change? In the former case the formula of the first complex telluride would be Na_2Te_2, while in the latter case its

[4] V. C. Allison, *Thesis*, Clark University, 1916.

[5] F. W. Power, *ibid.*, Clark University, 1917.

[6] At low concentrations, the ratio of tellurium to sodium in the solution would, of course, diminish if the solubility of the normal telluride, Na_2Te, were appreciable. The solubility of the normal telluride, however, is extremely low, for which reason, at higher concentrations, this ratio in solutions which are in equilibrium with the normal telluride remains fixed.

formula would be NaTe. That is, we should in one case have the complex telluride ion $Te^{--}Te$ with 2 negative charges, and in the second case the ion Te^{-} with a single negative charge. It is by no means obvious that the latter process may not occur. So far, we have so little information regarding complex compounds of this type that it would be unsafe to draw any definite conclusion without further data.

If the complex telluride ion carries 2 charges, then obviously the formula of the compound will be $Na_2Te^{--}Te_x$. By means of molecular weight determinations it should be possible to distinguish between the alternative possibilities suggested above. According to Franklin and Kraus,[7] the molecular weight of salts in ammonia solution at ordinary concentrations is practically normal, which corresponds roughly with their electrical properties, since their ionization at ordinary concentrations is comparatively low. It might be expected, therefore, that the molecular weight of the complex tellurides could be determined in ammonia solution. As Kraus has already pointed out,[8] the only readily available method for determining molecular weights in ammonia solution is that of determining the vapor-pressure change due to the solute. In the following investigation, therefore, this method has been adopted for the purpose of determining the molecular complexity of the complex tellurides in ammonia solution.

Apparatus and Experimental Method

The experimental method employed in this investigation is essentially the same as that employed by Kraus in determining the molecular weight of sodium in liquid ammonia solution. The apparatus employed consists essentially of 4 parts: first, a thermostat, by means of which the temperature may be maintained constant to 0.001° or better; second, a device for measuring accurately pressure differences of the order of magnitude of 1.0 mm. of mercury; third, the containing vessels for the solutions and the solvent, together with means for agitating the liquids; and fourth, a means of introducing known amounts of the metals and of ammonia into the containing vessel.

The Thermostat.—It is essential that the temperature be kept below that of the surroundings; otherwise the solvent will distil into the cooler parts of the apparatus. Cooling was accomplished by allowing cold tap water to flow continuously through a 3-meter length of copper tubing of 5 mm. internal diameter. This tube was immersed in the thermostat liquid, as will be described more in particular below.

The desired temperature was maintained by means of a steel encased mercury thermo-regulator and an electrically heated coil of heavy resistance wire. The copper cooling tube, in the form of a flat spiral, and the heating element, of bare Nichrome wire wound in spiral form, were placed concentrically around the shaft of the stirrer and just above a cylindrical tube in which the stirrer revolved. It was found necessary to maintain very vigorous stirring. The thermostat contained approximately 110 liters of

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[7] Franklin and Kraus, *Am. Chem. J.*, **20**, 837 (1898).

[8] Kraus, *J. Am. Chem. Soc.*, **30**, 1197 (1908).

kerosene. Even though the thermostat seemed to be regulating well within 0.001°, it was found impossible to obtain consistent readings of the pressure. Apparently, the tubes containing the pure ammonia and the ammonia solution of the telluride were subject to temperature fluctuations due, in part at least, to incomplete mixing of the liquid in the thermostat. Increasing the stirring through the introduction of additional stirrers did not prove effective.

In order to overcome this difficulty, a square box *C*, of which a section is shown in Fig. 1, 11.5 x 30.5 cm. internal dimensions, constructed of 1cm. asbestos board, and provided with a chimney projecting 6 mm. above the liquid in the thermostat, was then placed around the containers *A* and *B* as shown in the figure. All the joints in this

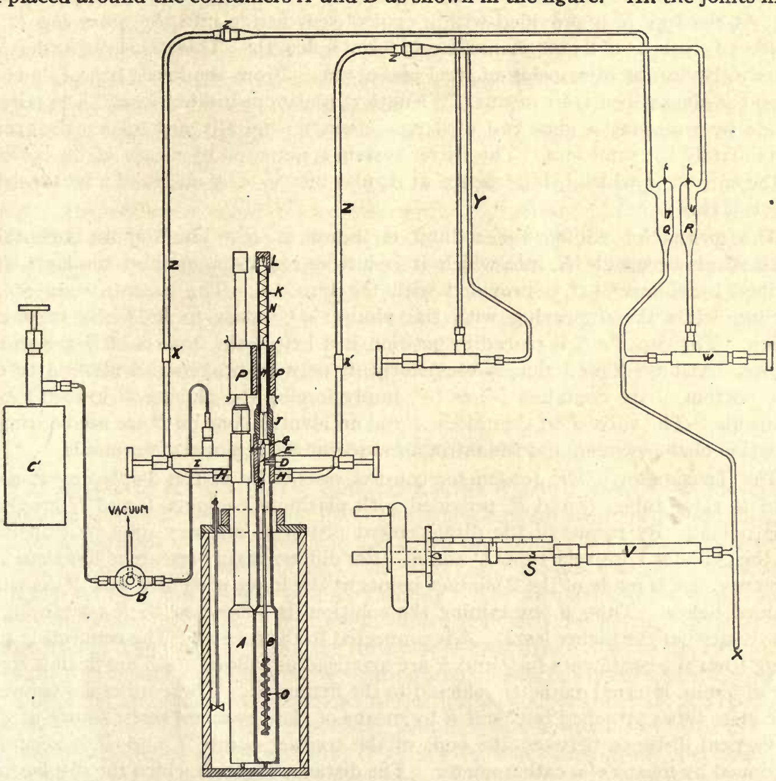

Fig. 1.—Apparatus employed in determining the vapor-pressure lowering due to complex tellurides dissolved in liquid ammonia.

box were made tight so that no liquid passed in or out. The liquid in this box was stirred vigorously by means of a small propeller, driven from the same motor as that which drove the large stirrer in the main thermostat. With this arrangement it was found possible to obtain reasonably consistent readings. The box served to integrate the temperature fluctuations in the main thermostat in the immediate neighborhood of the containers *A* and *B*.

The Containers.—The general scheme of the apparatus is shown in Fig. 1. *A* and *B* are the containers. These are identical in every respect except that *B* is fitted with a means, shown at *D*, for introducing the sodium into the ammonia. The tube *B* is shown in section. The containers are constructed of steel, and are lined with glass

nearly up to the hexagonal connecting piece to which H is attached. The steel shell has a thickness of approximately 0.8 mm. and the glass lining is of approximately the same thickness. The upper part of B, to which the movable plunger D is attached, is constructed of 2.5cm. hexagonal steel stock. This hexagonal portion is provided with 2 outlets. One of these outlets, into which H is screwed, leads to the pressure-measuring device; the other is fitted with a valve similar to I, shown attached to A in the figure. Each container consists of 2 parts which are screwed together, a tight joint being obtained by means of the conical seat shown at G. The upper portion of A, as of B, consists of the short 22mm. hexagonal steel section J to which is screwed and soldered the brass tube K. This tube has an internal diameter of 1 cm. and a wall thickness of 1.5 mm. At the top, K is provided with a conical seat fitting into the brass cap L. M is a piece of steel rod of 8 mm. diameter and 9 cm. in length. This rod is suspended from the cap L by means of a spring of steel piano wire. From the lower end of M is suspended the glass stirrer O by means of a length of platinum-iridium wire. The stirrer O is made by wrapping a glass rod of 3 mm. diameter spirally around another rod of approximately the same size. The stirrer system is actuated by means of the solenoids PP, the current in which is interrupted at regular intervals by means of a motor-driven contact device.

The means for adding the sodium is shown at D. The sodium is contained in a small glass capsule E, into which it is introduced by a method similar to that described by Kraus.[8] B is provided with the lugs LL. The capsule rests on the lower lug, while the upper lug with the plunger D serves to hold the capsule in position. The capsule E is placed in position just before the 2 parts of B are screwed together. At any desired time subsequently, it may be broken and allowed to drop to the bottom of the container below by simply forcing the plunger D inward against the capsule. The valve I on Container A and an identical one on B are used during the evacuation of the system, and the introduction and the removal of ammonia.

The Tensimeter.—The tensimeter consists essentially of the displacement piston S and 2 glass tubes Q and R, provided with platinum contacts T and U ground to needle points. By means of the displacement piston S, mercury may be transferred from the cylinder V into the tubes Q and R. For differences in pressure of less than 2 cm. of mercury, use is made of the 2 contact points at the lower ends of T and U, as will be explained below. Tube B, containing the solution, is connected to R containing the point situated at the higher level. A is connected to the tube Q. The connecting tubes leading from the containers to Q and R are arranged as follows. ZZ are flexible copper tubes of 5 mm. internal diameter soldered to the fittings H. These tubes are connected to the glass tubes attached to Q and R by means of glass to metal seals[9] shown at $Z'Z'$. The vertical distance between the ends of the contact points T and U is accurately determined by means of a cathetometer. The distance through which the displacement piston S moves in order to carry the mercury in Q and R from the level of the lower point to that of the upper point is accurately determined and is indicated on a scale S placed alongside the piston. This scale is divided into 32nds of an inch (0.8 mm.). A dial on the nut, which rotates once when the piston moves through a distance equal to one scale division, is divided into 100 divisions, and this serves accordingly to divide each $^1/_{32}$ inch into 100 parts. Contact between the platinum points and the mercury in the tubes Q and R is indicated by means of a telephone receiver placed in a circuit containing a small induction coil. This arrangement makes possible reading pressure differences with a precision of 0.01 mm. of mercury.

In order to read the difference in the level of the mercury surfaces in Q and R, the following procedure is carried out. Contact is first made with the lower

[9] Kraus, U. S. pat. 1,046,084, Dec. 3, 1912.

contact point in Q and the reading of the position of the piston S is noted on the adjacent scale. Mercury is now injected or withdrawn from Q, and R, depending upon whether the difference in pressure is less or greater than the distance between the points, until the upper meniscus makes contact with the point in R. For example, to obtain the actual value of the difference in pressure on the 2 surfaces when this is less than the distance between the 2 points, the equivalent height of mercury injected at S is subtracted from the distance between the points. When the difference in pressure is greater than that between the points, the equivalent height of mercury withdrawn is added to the distance between these points.

Pressure differences greater than 2 cm. of mercury are determined by reading directly the position of the menisci in Q and R by means of a cathetometer. A sheet of polished metal placed behind the meniscus, with strong illumination from the front, gives a very sharply defined outline of the meniscus when viewed through a telescope. Readings with the cathetometer under these conditions could readily be reproduced with a difference of less than 0.05 mm. of mercury.

Valve W serves to separate the 2 limbs of the manometer system, Q and R, when desired. An auxiliary mercury displacement piston, not shown in the figure, is connected at X. This piston has a capacity approximately 4 times that of S and is employed to adjust the surfaces in Q and R to any desired initial point. At Y is shown an auxiliary manometer, which serves to indicate the relative pressures in the system when these pressure differences are very large, as they often are when ammonia is withdrawn from the tubes containing the solution or the pure solvent.

The arrangement for introducing ammonia into the containers will be described in connection with the experimental procedure.

Experimental Procedure

The glass-lined portions of the containing tubes A and B are thoroughly cleaned with hot chromic acid cleaning mixture. The exposed metal portions of the containers, the internal portions of the valves, and the metal connections are washed with alcohol and ether and wiped clean with cotton. The tellurium,[10] in stick form, is introduced into the glass-lined tube B immediately after cleaning. The capsule E, containing a known quantity of sodium, is placed in position as shown at D, and B is closed by means of the screw joint G. The tubes A and B are then placed in position, A in its permanent position in the thermostat and B in a convenient position in which it may be surrounded with a bath of liquid ammonia. Connections to the flexible copper tubes ZZ are then made by soldered joints $X'X'$. The ammonia is contained in a light steel cylinder C'. This ammonia is purified by distillation into C' from a tank in which it has previously been purified by the methods described by Franklin and Kraus.[11] C' is connected to a valve D' by means of a length of flexible copper tube. The valve D' allows of connections being made with the vacuum system, when desired. A second flexible tube leads from the opposite side of D' to the valve I. This arrangement makes possible the evacuation of the connecting tubes between C' and either container A or B. Such an arrangement was found necessary when it was desired to introduce ammonia into A or B without evacuating the entire system.

In order to introduce ammonia into the container A, the procedure is as follows. C' is accurately weighed and connected to D' by means of a conical compression joint. The valve I is opened and A, together with all its connections, is evacuated. When the pressure has fallen to a few thousandths of a millimeter of mercury, Valve D'

[10] The tellurium employed in this investigation was prepared in connection with an earlier investigation in this Laboratory. See Kraus and Chiu, Ref. 3.

[11] Franklin and Kraus, *Am. Chem. J.*, **23**, 284 (1900).

is closed and the valve on C' is opened. The cylinder C' rests on a platform balance and is surrounded by a light electrical heater of tubular form. Approximately the desired quantity of ammonia is now distilled into A from C'. The valve I is then closed, C' is disconnected and weighed, and thus the exact amount of ammonia introduced into A may be obtained.

The expanded portions of A and B have a capacity of approximately 100 cc. About 60 g. of ammonia is introduced into A and B. About $^1/_3$ of this is blown into water contained in a 1000cc. flask, the exact amount of ammonia thus removed being determined by weighing the flask before and after the absorption of ammonia gas. This removal of ammonia was found necessary in order to insure complete elimination of foreign gases from the system. A trace of foreign gas on either side of the system has an appreciable influence on the pressure difference when this difference reaches a value of a few millimeters of mercury.

The introduction of ammonia into B is carried out in a manner similar to that already described in the case of A. The tube B is outside the thermostat, and with all its connections, including Q, is thoroughly evacuated before the ammonia is introduced. The lower portion of B is then introduced into a bath of boiling ammonia contained in a Dewar flask. About 5 g. of ammonia is now distilled from C' into B. The capsule E containing the sodium is then broken and allowed to drop into the ammonia in the container B. This container is then shaken for a period of 30 minutes in order to facilitate the initial reaction between the sodium and the tellurium. The bath of liquid ammonia in the Dewar flask is then removed and when B has come nearly to room temperatures it is placed in position in the thermostat as near to container A as possible; 55 g. of ammonia is now distilled into B in addition to that already introduced and about $^1/_3$ of this ammonia is blown off, as has already been described in connection with the procedure in filling A. This then gives the first concentration of the sodium-tellurium complex, for which measurements on the pressure difference are carried out. After having determined the difference in pressure between the solution and the pure solvent at this concentration, further quantities of ammonia are removed, the amounts being accurately determined by absorption in water and weighing. In this way the vapor pressure of the solution, relative to that of the pure solvent, is determined at a series of concentrations. The ammonia present in the container at the last concentration is determined by absorption in water and all concentrations are calculated back from this value.

In the first attempts to carry out the reaction between the sodium and the tellurium in B, the tube B was placed in position in the thermostat and ammonia was condensed in this tube at the temperature of the thermostat, 18°. Under these conditions, it was found that hydrogen is evolved when the sodium is dropped into the ammonia, owing to the formation of sodium amide. As a result it was found impossible to determine the true vapor pressure of the solution. In order to overcome this difficulty, the reaction was carried out at the temperature of boiling liquid ammonia, as has just been described.

It is necessary to correct for the quantity of ammonia present as vapor above the surface of the liquid and in the various connecting tubes. This quantity was determined by filling the apparatus with ammonia vapor under the pressure existing in the cylinder C'. The weight of this ammonia was obtained by weighing C'. Knowing the mass of ammonia present, the temperature and pressure, it was possible to calculate the corrections within the necessary limits of precision. In applying the correction at the various concentrations, the volume of liquid ammonia was subtracted from the total volume of the apparatus as determined. The above method of correction is not entirely accurate; but, in view of the fact that the correction in any case is very small, it was found unnecessary to determine the correction with a greater degree of precision.

After the completion of an experiment at a series of concentrations with a given quantity of sodium, ammonia is again introduced into the container B, which still con-

tains the sodium-tellurium compound, and a new set of readings is made at a series of concentrations.

The amount of ammonia in the container A, about 30 g. as a rule, was maintained constant during an experiment.

Experimental Results

The results of all experiments carried out in the manner described are given in the following table. At the head of each sub-table is given the

TABLE I

VAPOR-PRESSURE LOWERING OF SOLUTIONS OF THE COMPLEX SODIUM TELLURIDE AT DIFFERENT CONCENTRATIONS

Liquid ammonia G.	$\frac{n}{n+N} \times 10^4$	ΔP Mm. Hg	$\frac{\Delta P}{P} \times 10^4$	Ratio $\frac{\Delta P}{P} / \frac{n}{n+N}$
Series 1, 0.1113 g. of Na, 17.9°				
31.386	26.2	8.19	13.6	0.54
21.186	38.8	12.54	20.9	0.54
15.536	52.7	17.27	28.7	0.54
10.261	79.8	26.05	43.2	0.54
6.446	126.0	39.07	65.6	0.52
Series 2, 0.055 g. of Na, 17.9°				
42.198	9.63	2.42	4.1	0.43
13.582	29.9	10.25	17.0	0.56
8.897	45.6	14.56	24.2	0.53
Series 3, 0.055 g. of Na, 17.9°				
25.648	15.8	4.64	7.7	0.49
17.348	23.4	7.35	12.2	0.52
10.916	37.4	12.60	20.9	0.56
Series 4, 0.055 g. of Na, 19°				
37.721	10.8	3.07	4.9	0.46
27.166	15.0	5.16	8.28	0.55
15.876	25.6	8.99	14.4	0.56
10.366	39.1	14.28	22.9	0.58
Series 5, 0.1398 g. of Na, 19°				
40.041	25.8	7.60	12.2	0.47
30.454	33.8	10.9	17.5	0.52
19.384	53.0	17.2	27.7	0.52
14.314	71.7	22.9	36.9	0.50
9.154	112.0	35.9	57.7	0.51
Series 6, 0.1398 g. of Na, 20°				
38.909	26.5	8.2	12.8	0.48
28.767	35.9	12.0	18.7	0.52
20.904	49.3	17.0	26.5	0.54
15.272	67.3	22.8	35.5	0.53
11.362	90.6	32.0	49.8	0.55

number of the series of the experiment, the weight of sodium employed in the series in question, and the temperature at which the experiment was carried out. In the first column is given the weight of liquid ammonia;

in the second column, the value of the molal fraction, $\frac{n}{n+N} \times 10^4$; in the third column, the pressure difference, ΔP, in millimeters of mercury; in the fourth column, the relative pressure difference, $\frac{\Delta P}{P} \times 10^4$; and in the fifth column, the ratio $\frac{\Delta P}{P}/\frac{n}{n+N}$.

Discussion

The purpose of this investigation was to determine the complexity of the telluride in solution. Since even the binary salts are relatively slightly ionized at concentrations in the neighborhood of 0.1 N and since, in general, the ionization of salts of higher type is much lower than that of typical binary salts, it follows that the ionization process of the dissolved telluride might be expected to have little influence on the observed vapor-pressure change. In order to determine the complexity of the telluride, the molecular weight of the dissolved complex must be determined. It is, of course, obvious that in such a determination the true molecular weight of the dissolved compound is not obtained in any case, but merely the number of moles of dissolved substance in the mixture. If the laws governing dilute mixtures hold, then the number of moles of solute for any given composition of the mixture may obviously be determined from the relative vapor-pressure change of the solution, according to Raoult's law. Whether or not the conditions of dilute systems are fulfilled in solutions of electrolytes at a given concentration cannot be predetermined. If, however, the relative lowering of the vapor pressure can be determined at a series of concentrations, some inference may be drawn as to whether the conditions of a dilute system are fulfilled in a given case from the manner in which the vapor pressure varies as a function of the concentration at low concentrations. If Raoult's law holds, then obviously $\frac{\Delta P}{P} = \frac{n}{n+N}$. In other words, the ratio $\frac{\Delta P}{P}/\frac{n}{n+N}$ equals unity, and a plot of the observed values of $\Delta P/P$ against those of $\frac{n}{n+N}$ should yield a straight line, the tangent of whose slope is unity. If the laws of dilute solutions are not fulfilled, then a plot of the values of $\Delta P/P$ against the fractional composition will lead to a curve which, at sufficiently low concentrations, where the deviations from the laws of dilute solutions become small, approaches the theoretical straight line asymptotically. From vapor-pressure determinations at a series of concentrations, therefore, it is possible to reach a conclusion as to whether or not the laws of dilute solutions are fulfilled within the limits of experimental error.

In the preceding table, n is the number of atoms of sodium and N the

number of moles of ammonia in the mixture. If the complex telluride contained only a single atom of sodium in the molecule, the value of the ratio $\frac{\Delta P}{P}/\frac{n}{n+N}$ should be unity; while, if 2 atoms of sodium were present in the molecule, the ratio should have a value of 0.5.

In Col. 5 of the table are given the values of the ratio $\frac{\Delta P}{P}/\frac{n}{n+N}$ for different concentrations of the solution. An inspection of the table will show that this ratio has a value in the neighborhood of 0.5. In Fig. 2 the values of $\frac{\Delta P}{P} \times 10^4$ are plotted against values of $\frac{n}{n+N} \times 10^4$. While there is considerable variation among the various points due to errors which

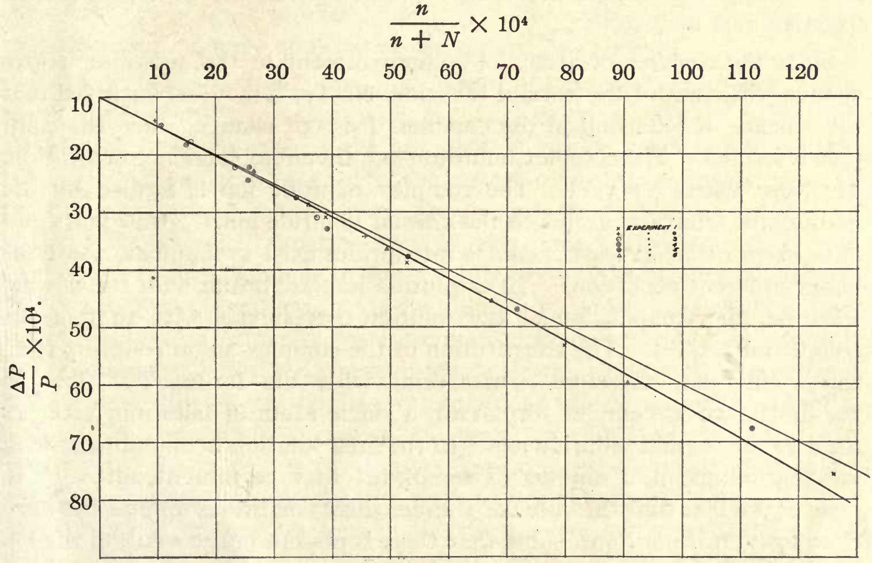

Fig. 2.—The variation of the vapor pressure of the sodium-telluride solution as a function of composition.

could not be eliminated entirely, it is clear that the points determine a curve which approaches an asymptote for which $\frac{\Delta P}{P}/\frac{n}{n+N}$ has a value 0.5. The straight line appearing in the figure represents this asymptote. In the more dilute solutions, the points follow this theoretical curve within the limits of the experimental error, but at higher concentrations the deviations from this curve become appreciable, although the deviations are nowhere large. The mean value of the ratio $\frac{\Delta P}{P}/\frac{n}{n+N}$ is 0.52, with a maximum variation from 0.43 to 0.58. The higher values of the ratio

at the higher concentrations are doubtless in part due to deviations from Raoult's law, while at lower concentrations they are probably in the main due to experimental errors. At the lowest concentrations, the total volume occupied by the solution was approximately 80 cc., under which conditions it is difficult to establish equilibrium between the liquid and the vapor phase. At the same time, at these concentrations, the total pressure change is of the order of magnitude of 3 mm. On the whole, the results are as concordant as might be expected, in view of the conditions under which the experiments were carried out. The lowest concentration is approximately 0.03 *N*. The results show conclusively that 2 atoms of sodium are present per molecule of the complex telluride whose composition, therefore, is represented by the formula Na_2Te_x, where, according to the measurements of Kraus and Chiu, x varies from 3.8 at concentration 0.084 to 4.04 at 2.45.[12]

Since the number of atoms of sodium present in the molecule corresponds with that of the normal telluride, Na_2Te, it may be concluded that the valence of tellurium in the complex does not change, when the complex is formed. The complex tellurium ion, therefore, has the constitution, $Te^{--}Te_y$, where $y=x-1$. The complex telluride ion is formed by the addition of tellurium atoms to the normal telluride ion. Kraus and Chiu have shown that at least 2 complex tellurides exist in ammonia solutions under different conditions. In a solution in equilibrium with the normal telluride, the composition of the solution corresponds with that of the compound Na_2Te_2. The constitution of the complex anion resulting from this compound, therefore, corresponds with the formula $Te^{--}Te$. In the first stage of complex formation, a single atom of tellurium attaches itself to the normal telluride ion. In the final solution in equilibrium with metallic tellurium, a number of complexes may be present, although in view of the fact that the value of x under these conditions approaches very close to 4.0 it is not improbable that there is present in the solution the ion $Te^{--}Te_3$.

Since the valence of the telluride ion in the complex is the same as that of the normal telluride, the valence of the telluride ion does not change on formation of the complex. This has an important bearing on our conceptions of the constitution of complex ions of this type. As has already been pointed out, other of the less electropositive heavy elements, such as lead, tin and antimony, form complex compounds with the alkali metals which resemble the complex tellurides in many respects. In the case of antimony, the initial compound formed is Na_3Sb and there is evidence indicating that the initial compound formed with lead is Na_4Pb. In the case of the latter element, however, the normal plumbide is not stable with respect to the complex and free metallic sodium in solution, decomposition occurring ac-

[12] The concentration is expressed in atoms of sodium per liter of pure ammonia.

cording to a reaction of the type: $Na_4Pb \longrightarrow Na + NaPb_x$. In the presence of excess lead the ultimate composition of the solution corresponds with that of the compound $Na_4Pb.Pb_8$. The normal plumbide has a constitution corresponding to the formula Na_4Pb, and, in view of the behavior of the telluride solutions, it may be inferred that the valence of the plumbide ion remains unchanged in the complex. On the other hand, without an actual determination of the molecular weight of the plumbides in solution, it cannot be definitely stated that the negative valence of the plumbide ion may not vary from complex to complex. It is, of course, well known that the positive valence of certain elements, such as lead, for example, varies with conditions; and it is, therefore, conceivable that a similar variation may occur in the case of the negative valence of metallic elements. It appears unlikely, however, that a change of the negative valence occurs on mere addition of the element in question.

As has been pointed out by Kraus in an earlier paper,[13] the results obtained from a study of the various complexes in liquid ammonia, and particularly of the complex tellurides, have an important bearing on our conceptions as to the nature of metallic compounds. In the first place, there is clearly brought to view the important property of elements, in general, of functioning as negative ions. This property is common to the typical elements of the seventh, sixth, fifth and fourth groups, and possibly to certain elements of the third. That is, it has been definitely shown that these elements form complex compounds which are soluble in liquid ammonia and that, in solution, the more electronegative element is associated with a negative charge. In order to account for the properties of metallic compounds, therefore, we must take into account, first, the tendency of the more electronegative elements in their compounds to act as negative ions; and, second, the tendency of the negative ions of these elements to form complex ions in the presence of larger amounts of the same elements. The electrochemical properties of these compounds in ammonia solution clearly show that in solution they possess all the properties characteristic of electrolytes, that is, of salts; and there is apparently nothing to differentiate solutions of these compounds from ordinary salts in the same solvent under similar conditions. These compounds in solution, therefore, are in fact salts. In solution they differ from other salts with which we are familiar only in that the negative ion is complex with its composition dependent upon conditions, while in the case of most salts the negative ion has a fixed composition. Nevertheless, although these compounds are true electrolytes or salts in solution, in the free state, they exhibit, for the most part, characteristic metallic properties. In general, the metallic properties of these compounds are the more pronounced, the less electronegative the negative constituent, and the less electropositive

[13] Kraus, *J. Am. Chem. Soc.*, **44**, 1216 (1922).

the positive constituent. Thus, the normal telluride is entirely non-metallic, while the normal antimonide is a metal. So, also, the sulfides of the alkali metals are non-metallic while those of heavy metals are metallic. The lower the atomic weight of the electronegative element in a given group of elements, the less pronounced are the metallic properties of its compounds. Thus, the normal phosphides of the alkali metals are non-metallic.

It should be noted, also, that no considerable reaction occurs between the solvent and the metallic compound when the process of solution takes place. The energy effects accompanying solution are apparently of a very low order of magnitude, thus indicating that no fundamental reaction occurs in which the character of the compound in solution is materially altered from that in the solid state. It may be inferred, therefore, that metallic compounds between strongly electropositive elements, such as the alkali metals, and the less electropositive elements such as lead, tin, etc., have a salt-like structure; that is, they possess an ionic constitution. In this way it is possible to account for many of the properties of metallic compounds which otherwise cannot readily be reconciled with present conceptions as to the constitution of elementary substances.

One of the striking features of the interaction between a given pair of metallic elements is the large number of compounds derivable from a single such pair of elements. Such compounds cannot be accounted for on the basis of any of the accepted theories of valence or of atomic structure. Taking into account, however, the tendency of the less electropositive metallic elements to form negative ions and, furthermore, the tendency of these ions to form complexes, compounds of this type are readily accounted for and may be harmonized with present views of atomic structure. Every element, thus, has an electropositive, as well as an electronegative valence. The negative valence is one for the seventh group of elements and increases by one in passing to an adjacent group from left to right, just as the positive valence increases in passing from group to group from right to left in the periodic table. The negative, as also the positive, valence is 4 for the fourth group of elements. Whether or not the negative valences may increase above 4 cannot be stated. The chief distinction between electronegative and electropositive valence, aside from the sign of the charge, is that the ions carrying a negative charge have a great tendency to form definite complexes with other atoms. The nature of the combination, in this case, is, at present, not understood. Nevertheless, we are dealing here with a phenomenon which is in no sense restricted to a small group of elements.

While the only metallic compounds whose constitution can be arrived at are those which are soluble in liquid ammonia, it does not follow that such an ionic constitution is restricted to compounds which are soluble.

It is possible, and indeed probable, that many, if not all, metallic compounds are of this type, the more electropositive constituent being present as a positive ion and the more electronegative constituent as a negative ion. In these compounds the electronegative constituent, at any rate, may be present in the form of a complex ion. Whether the positive constituent may likewise form a complex ion under suitable conditions cannot now be stated.

In the past the term "salt" has been restricted to non-metallic compounds having ionic constitution, namely, compounds exhibiting ionic properties in solution and in the pure state and showing no metallic properties. Metallic compounds, on the other hand, have practically not been classified, and, for the most part, have been sharply differentiated from the salts. According to the views here proposed, there is no sharp line of demarcation between the salts and metallic compounds. The property of metallicity is a more or less accidental one, depending, of course, upon the nature of the elements present in the compound, and particularly upon the relative electropositiveness and electronegativeness of the constituents. In other respects, however, there is nothing to indicate any marked break in the physical and chemical properties of binary compounds between two elements, as we pass from ordinary salts to true metallic compounds. If one constituent is strongly electropositive and the other constituent strongly electronegative, then the resulting compound is a typical salt which shows no metallic properties. As, however, the electropositiveness of one constituent and the electronegativeness of another constituent becomes less pronounced, the metallic characteristics become more accentuated and the resulting compounds exhibit metallic properties, except in the case of elements which are relatively very strongly electronegative and electropositive. Thus, practically all the compounds of the halogens with other elements are either salt-like or neutral substances. It is only seldom that they show metallic properties.[14]

In the case of elements of the sulfur group, the normal compounds with the alkali metals appear throughout to be non-metallic. Certain of the complex compounds, however, such as the tellurides, exhibit metallic properties even in the case of the alkali metals, as has already been noted. On the other hand, even the normal tellurides of the less electropositive elements, such as silver and lead, exhibit distinctly metallic properties. Indeed, we are not confined, here, to the tellurides; as is well known, the

[14] It is interesting to note in this connection that cuprous iodide is a typical salt-like substance, exhibiting purely non-metallic properties in the pure state. It absorbs iodine in the solid state, however, yielding a substance exhibiting metallic properties which are a function of the amount of iodine absorbed. The greater the amount of iodine present in this system, the more do the properties resemble those of characteristic metallic substances. [Baedeker, *Ann. Physik,* **22,** 765 (1907); **29,** 566 (1909). Baedeker and Pauli, *Physik, Z.*, **9,** 431 (1908).]

normal sulfides and even the oxides of many elements exhibit metallic properties in certain states as, for example, some of the iron oxides and some of the natural sulfides of lead. There is nothing to indicate that, in their constitution, these metallic compounds differ materially from similar non-metallic compounds which exhibit a salt-like structure. The structure of all such compounds, therefore, is essentially of the same type, corresponding to that of normal salts, while the metallic properties are determined primarily by the relative electropositiveness and electronegativeness of the elements concerned in the compound. Metallic compounds should, therefore, be classed with the salts.

Summary

1. The vapor pressure lowering due to the complex sodium-tellurium compound in liquid ammonia has been measured at a series of concentrations down to 0.03 N.

2. When the values of $\Delta P/P$ are plotted against values of $\frac{n}{n+N}$, where n is the number of atoms of sodium in the mixture, a curve results which in dilute solution approaches very closely to a straight line, for which the value of $\frac{\Delta P}{P}/\frac{n}{n+N}$ equals 0.5. Apparently Raoult's law is very nearly obeyed by solutions of the complex telluride in liquid ammonia, and from the value of the above ratio it follows that 2 atoms of sodium are present per molecule of the complex telluride present in solution. The complex telluride ion, therefore, carries 2 charges. The formation of the complex telluride consists in the addition of tellurium atoms to the normal telluride ion, the valence of the telluride ion undergoing no change under these conditions.

3. The bearing of this result on our conceptions of the nature of other similar complexes in ammonia solution and of metallic alloys in general is discussed.